PB-224 544

ORGANIC POLLUTANT IDENTIFICATION UTILIZING MASS SPECTROMETRY

ENVIRONMENTAL PROTECTION AGENCY

JULY 1973

DISTRIBUTED BY:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

W71 003

SELECTED WATER RESOURCES ABSTRACTS INPUT TRANSACTION FORM	1. Report No.	PB 224 544 W
ORGANIC POLLUTANT IDENTIFICATION UTILIZING MASS SPECTROMETRY,		5. Report Date 6. 8. Performing Organization Report No.
McGuire, J.M., Alford, A.L., Carter, M.H.		EPA Project 1-AON-25
~~U.S.~~ Environmental Protection Agency, National Environmental Research Center, Southeast Environmental Research Lab. Athens, Georgia		13. Type of Report and Period Covered
~~12 Sponsoring Organization U. S. Environmental Protection Agency~~		

Environmental Protection Agency, report ~~number~~ EPA-R2-73-234, July 1973. 55p. 11 fig, 5 tab, 16 ref

A system has been developed for the rapid identification of volatile organic water pollutants. It involves computer controlled gas chromatography/mass spectrometry with computerized matching of mass spectra. Application of this system to the analysis of waste effluents revealed a significant number of pollutants that were not previously known to be present. (EPA)

NATIONAL TECHNICAL INFORMATION SERVICE

17a Descriptors: *Pollutant Identification, *Organic Compounds, *Mass Spectrometry, *Gas Chromatography, *Computers, *Date Processing, *Organic Pesticides, Phenols

17b Identifiers: ~~*GC/MS~~, ~~*Computer Controlled~~, *Computer Matching, Coal Gasification Effluent, Synthetic Rubber Effluent, Pesticide Manufacturing Effluent

17c COWRR: 05A, 05B, 05C

19. Security Class. (Report)	21. No. of Pages	Send To:
20. Security Class. (Page)	22. Price	WATER RESOURCES SCIENTIFIC INFORMATION CENTER U.S. DEPARTMENT OF THE INTERIOR WASHINGTON, D.C. 20240

John M. McGuire | Southeast Environmental Res. Lab.

1

51

RESEARCH REPORTING SERIES

Research reports of the Office of Research and Monitoring, Environmental Protection Agency, have been grouped into five series. These five broad categories were established to facilitate further development and application of environmental technology. Elimination of traditional grouping was consciously planned to foster technology transfer and a maximum interface in related fields. The five series are:

1. Environmental Health Effects Research
2. Environmental Protection Technology
3. Ecological Research
4. Environmental Monitoring
5. Socioeconomic Environmental Studies

This report has been assigned to the ENVIRONMENTAL PROTECTION TECHNOLOGY series. This series describes research performed to develop and demonstrate instrumentation, equipment and methodology to repair or prevent environmental degradation from point and non-point sources of pollution. This work provides the new or improved technology required for the control and treatment of pollution sources to meet environmental quality standards.

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402 - Price 85 cents

W74. 00309

EPA-R2-73-234
July 1973

ORGANIC POLLUTANT IDENTIFICATION UTILIZING MASS SPECTROMETRY

by

John M. McGuire
Ann L. Alford
Mike H. Carter
Southeast Environmental Research Laboratory
College Station Road
Athens, Georgia 30601

Project #16ADN 25
Program Element #1B1027

NATIONAL ENVIRONMENTAL RESEARCH CENTER
OFFICE OF RESEARCH AND MONITORING
U. S. ENVIRONMENTAL PROTECTION AGENCY
CORVALLIS, OREGON 97330

1.6

EPA Review Notice

This report has been reviewed by the Environmental Protection Agency and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Abstract

A system has been developed for the rapid identification of volatile organic water pollutants. It involves gas chromatography/mass spectrometry with computerized matching of mass spectra. Application of this system to the analysis of waste effluents revealed a significant number of pollutants that were not previously known to be present.

CONTENTS

Section		Page
I	Conclusions	1
II	Introduction	3
III	GC/MS/Computer/Matching System	7
IV	Specific Pollutant Identifications . . .	15
V	Acknowledgments	29
VI	References	31
VII	Glossary	33
VIII	Appendix	35

Preceding page blank

FIGURES

Page

1. Schematic outline of Finnigan GC/MS/computer system 8

2. Comparison of parathion mass spectra from magnetic and quadrupole spectrometers 12

3. Flame ionization chromatogram of water extract 16

4. Reconstructed gas chromatogram of pesticide manufacturing plant effluent 17

5. Reconstructed gas chromatogram of plant effluent containing polychlorinated biphenyls 19

6. Limited mass reconstructed gas chromatogram of plant effluent containing polychlorinated biphenyls 21

7. Reconstructed gas chromatogram of synthetic pesticide mixture 22

8. Mass spectrum of p,p'-DDT from synthetic pesticide mixture 23

9. Reconstructed gas chromatogram of coal gasification plant extract 24

10. Computerized spectra matching program dialogue for a component of coal gasification plant extract 26

11. Reconstructed gas chromatogram of synthetic rubber plant effluent 28

TABLES

		Page
1.	Comparison of Compounds Reported by Discharger and Compounds Identified by EPA in Industrial Discharge	4
2.	Steps in GC/MS/Computer Analysis	10
3.	Compounds Identified in Pesticide Plant Effluent	18
4.	Identification of Trace Components in Synthetic Pesticide Mixture	20
5.	Compounds Tentatively Identified in Waste Effluent of Coal Gasification Pilot Plant . .	25

SECTION I

CONCLUSIONS

1. Combined gas chromatography and mass spectrometry is a powerful tool for identification of organic pollutants in the environment.

2. Utility and speed of this technique are enhanced when the mass spectrometer is computer controlled.

3. Computerized matching of pollutant mass spectra with spectra in the EPA/Battelle data base provides rapid identifications with minimal operator decisions.

4. The 11,000-spectra data base is not sufficiently comprehensive to identify all unknown pollutants.

SECTION II

INTRODUCTION

Setting and enforcing water quality criteria, determining the fate and effects of water pollutants, and developing optimum control measures require the capability for identifying specific organic pollutants. Table 1 dramatically illustrates the need to determine the composition of industrial wastes by chemical analysis. The compounds in the left column are those suspected by the discharger to be in his effluent based on his knowledge of products, raw materials and processes. The right column, based on chemical analysis of the effluent, contains over twice as many compounds.

The identification technique must be highly specific since thousands of compounds must be considered. Because some organic compounds are toxic to aquatic organisms at concentrations below 10 µg/ℓ, the technique must also be sensitive.

Gas-liquid chromatography (GC) has adequate sensitivity and reproducibility to provide excellent quantitation for volatile organics when the identity of the chemical is known. However, pollutant identifications obtained by comparison of relative retention times are subject to interferences and are questionable for the unknown mixtures found in natural waters. GC, however, may be used as a preliminary separation technique. The effluent may then be introduced into a different type of instrument for qualitative identification.

High resolution mass spectrometry provides the elemental composition of unknowns but present instruments are neither sensitive enough nor fast enough to monitor GC peaks. Infrared spectroscopy and nuclear magnetic resonance spectrometry provide specific identification but have low sensitivities.

Workers at the Southeast Environmental Research Laboratory showed the feasibility of using gas chromatography interfaced with low resolution mass spectrometry for unknown identification (1-4). They used an Hitachi RMU-7 mass spectrometer tuned for maximum

Preceding page blank

Table 1

Comparison of Compounds Reported by Discharger and Compounds Identified by EPA in Industrial Discharge

Products and Raw Materials Reported	Compounds Identified
Propylene	m-xylene*
Ethylene	p-xylene*
Butadiene	1,5-cyclooctadiene
Butane	o-xylene*
Octane	isopropylbenzene (cumene)
Ethylene glycol	styrene*
Ethylene oxide	o-ethyltoluene
Polyglycols	α-methylstyrene*
Ammonia	diacetone alcohol
Raw gas	indan*
Ethane	2-butoxyethanol
Refinery gases	β-methylstyrene
Refinery C_2 stream	indene*
Refinery C_3 stream	dimethylfuran isomer
Propane	n-pentadecane
Hydroformer gas	1-methylindene*
Platformer gas	3-methylindene
	acetophenone
	n-hexadecane
	α-terpineol
	naphthalene*
	α-methylbenzyl alcohol
	2-methylnaphthalene*
	benzyl alcohol
	1-methylnaphthalene*
	ethylnaphthalene isomer
	phenol*
	2,6-dimethylnaphthalene*
	methyl ethyl naphthalene isomer
	cresol isomer
	acenaphthene
	acenaphthalene
	methylbiphenyl isomer
	fluorene
	phthalate diester (undetermined)
	3,3-diphenylpropanol
	phthalate diester (undetermined)

*Identification was confirmed with a standard.

sensitivity, together with manual chart reading and data reduction. Many hours of applied effort are required to gather data, read charts, correct backgrounds, construct a data presentation for interpretation, and interpret the data. Because of this, manual GC/MS is too slow for effective identification of water pollutants.

Most time-limiting factors in manual GC/MS can be accomplished by a computer. To evaluate the feasibility of this approach, a computerized system was obtained in 1971. A mini-computer in this system controls the operation of a quadrupole mass spectrometer and associated output devices. At the same time, a project was started to develop a computerized program for interpretation of the resulting mass spectra.

SECTION III

GC/MS/COMPUTER/MATCHING SYSTEM

Computerized GC/MS produces many mass spectra from a single environmental sample (5). Interpretation of these spectra is time-consuming. To make the technique usable by all enforcement laboratories, an EPA research grant was made to Battelle Memorial Institute to develop a computerized spectra matching program and a reference library of organic pollutant spectra. The program (6) being developed is a very useful tool, providing identification of an unknown spectrum within one minute.

This GC/MS/computer/spectra-matching system has been selected by the Contaminants Characterization Program as the best current means for rapid identification of organic contaminants in water.

Instrumentation

The GC/MS/computer system now used at the Southeast Environmental Research Laboratory for semi-automatic pollutant identification is outlined in Figure 1. The GC is a modified Varian 1400 chromatograph with a temperature controlled oven that can be programmed from 50° to 500° C. It has no independent detector and serves only as a specialized inlet to the mass spectrometer.

The all-glass, single-stage Gohlke jet separator enriches organic samples by utilizing differences in diffusion rates of sample and carrier gases in a turbulent jet.

The Finnigan 1015 mass spectrometer is a quadrupole instrument with three mass ranges extending to m/e 750. It is capable of unit resolution throughout the range (e.g., 1/20 at mass 20 and 1/625 at mass 625). Therefore, instrument sensitivity at low mass is much higher than in a magnetic instrument. At a scan speed of 120 amu/sec, sensitivity is adequate to give

Preceding page blank

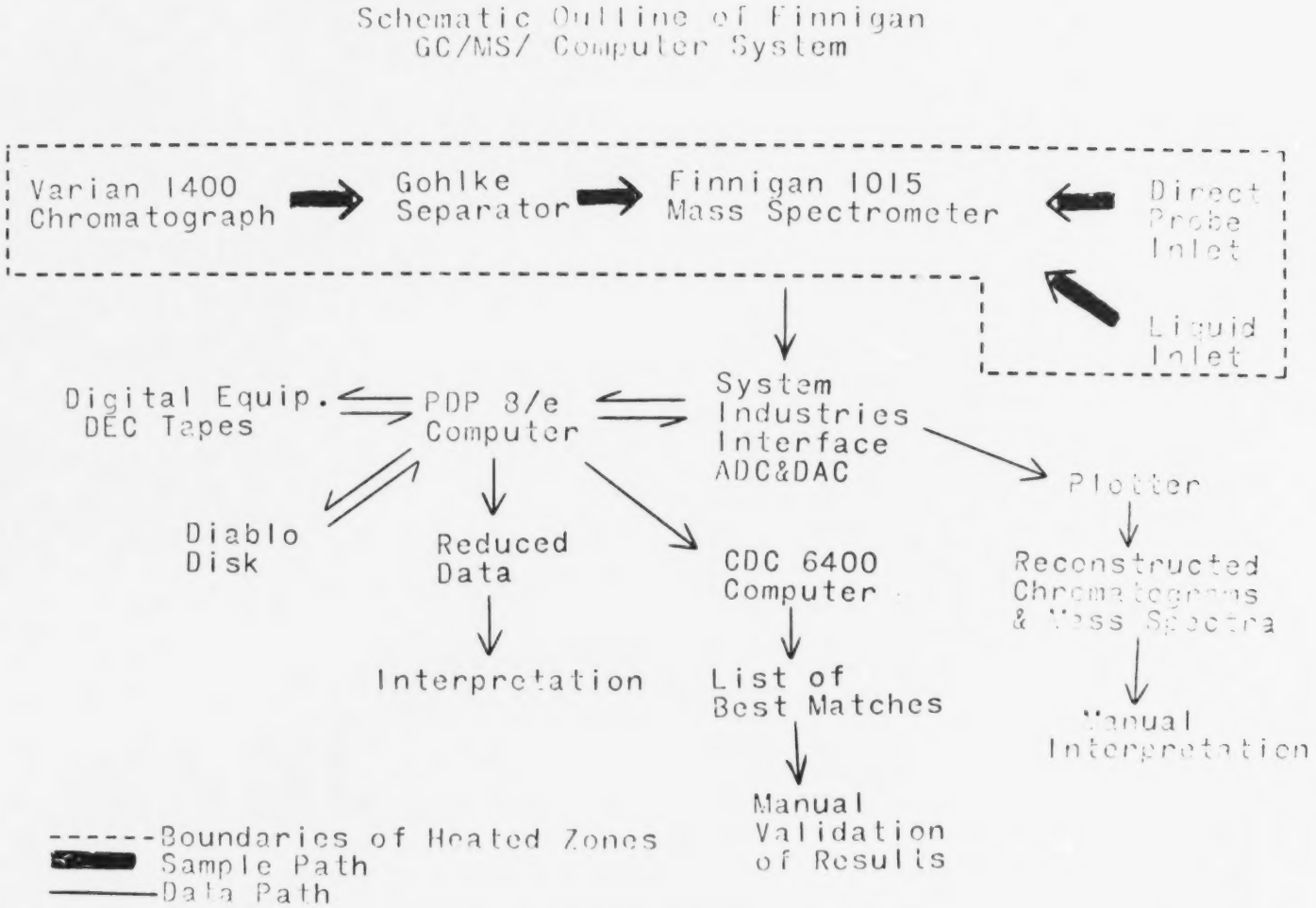


FIGURE 1. Outline of Finnigan GC/MS/Computer System

identifiable spectra for 20 ng of material introduced into the GC inlet.

The liquid inlet is used for introduction of calibration compounds, the direct probe for solid materials.

The System Industries interface, the analog-to-digital converter, and the digital-to-analog converter permit the Digital Equipment Corporation (DEC) computer to control the mass spectrometer during calibration and data acquisition; to accept data from the mass spectrometer; and to control the Houston plotter during data reduction.

The DEC PDP8/e computer, which is the heart of the data system, has a 4096 word core and an ASR33 teletypewriter. Programs, raw data, and reduced data are stored on either the two DECtape units or the Diablo disc. Output of the reduced data is achieved under computer control via the plotter, the teletypewriter, or a coupling device. The coupling device connects the PDP8 to the central CDC 6400 computer and permits semi-automatic spectrum identification by the matching program.

Using this system, data reduction times are much less than for the manual reduction methods formerly used. Only 30 minutes of applied operator time is required to create the instruction string needed to output reduced data for a 20-peak chromatogram. Data reduction time ranges from slightly more than one hour for the disc system to more than two hours for the tape system. Manual data reduction would require approximately 12 hours. The GC/MS/computer analytical procedure outlined in Table 2 works well; however, two obvious improvements are needed. The first is faster data output utilizing a cathode ray tube, and the second is a modification to permit time-shared use of the PDP8 for simultaneous acquisition and processing of data. With these modifications, overall data reduction time could be reduced by half.

Table 2

Steps in GC/MS/Computer Analysis

1. Formation of amu reference calibration file
2. Data acquisition
3. Plot of reconstructed gas chromatogram
4. Manual selection of GC peak and background spectra
5. Creation of background corrected spectra files
6. Output of spectra to central computer for data interpretation by spectra matching program
7. Manual inspection of match results

Matching Program

Matching schemes of varying complexity have been described in the literature. All rely on a set of representative reference spectra. In the case of the most complex deductive programs, such as the DENDRAL program (6-8) developed at Stanford, the data base need not be extensive, but must be comprehensive. In the case of comparative systems (9, 10) the data base must include a spectrum of the unknown compound.

Widespread use of GC/MS/spectra-matching in pollutant identification would require rapid matching, an indication of the similarity of the unknown spectrum to the reference spectrum for each match, and easy access to a central spectra library. The algorithm of a matching program described in the literature (11) was selected as the basis for the EPA matching program. The rapid program developed jointly by Battelle and the Southeast Environmental Research Laboratory centered around this algorithm and a CDC 6400 time-shared computer (12).

The EPA/Battelle matching program, taking advantage of the high information redundancy of mass spectra, is based on the two most intense peaks in every 14 mass units. There are four main steps in the matching process:

- screening based on molecular weight range,
- screening based on the most intense peak of the unknown spectrum,
- pre-searching based on the spectrum family, and
- ordering of best matches based on peak-by-peak comparison of the unknown spectrum with those reference spectra passing the pre-search.

To reduce operator time and eliminate human errors and prejudices in selecting, formatting, and transmitting data, PDP8 utility routines transfer input spectra data directly from the user's remote PDP8 to the central CDC 6400. These programs have been evaluated and improved during the past year.

A match against the present data base of 11,000 spectra (10,600 general organic spectra from the Aldermaston collection and 400 pollutant spectra from the Southeast Environmental Research Laboratory and Battelle,) requires approximately 45 seconds.

The "similarity index" (S.I.) gives the user an immediate indication of the quality of the matches. The "best hit" will be the first identification; the S.I. will show whether it is a poor match (<0.2 if the data base does not contain any closely related compounds), one of several fair matches (0.2-0.35 if the correct compound is not in the data base but related ones are), or a good match (>0.35 if the S.I. of the second best hit is significantly lower.)

Compared with magnetic deflection spectrometers, quadrupole instruments exhibit a bias toward low mass. This is demonstrated in Figure 2, which compares both types of spectra for the pesticide, parathion. Since the Aldermaston data base is comprised primarily of spectra obtained on magnetic deflection mass

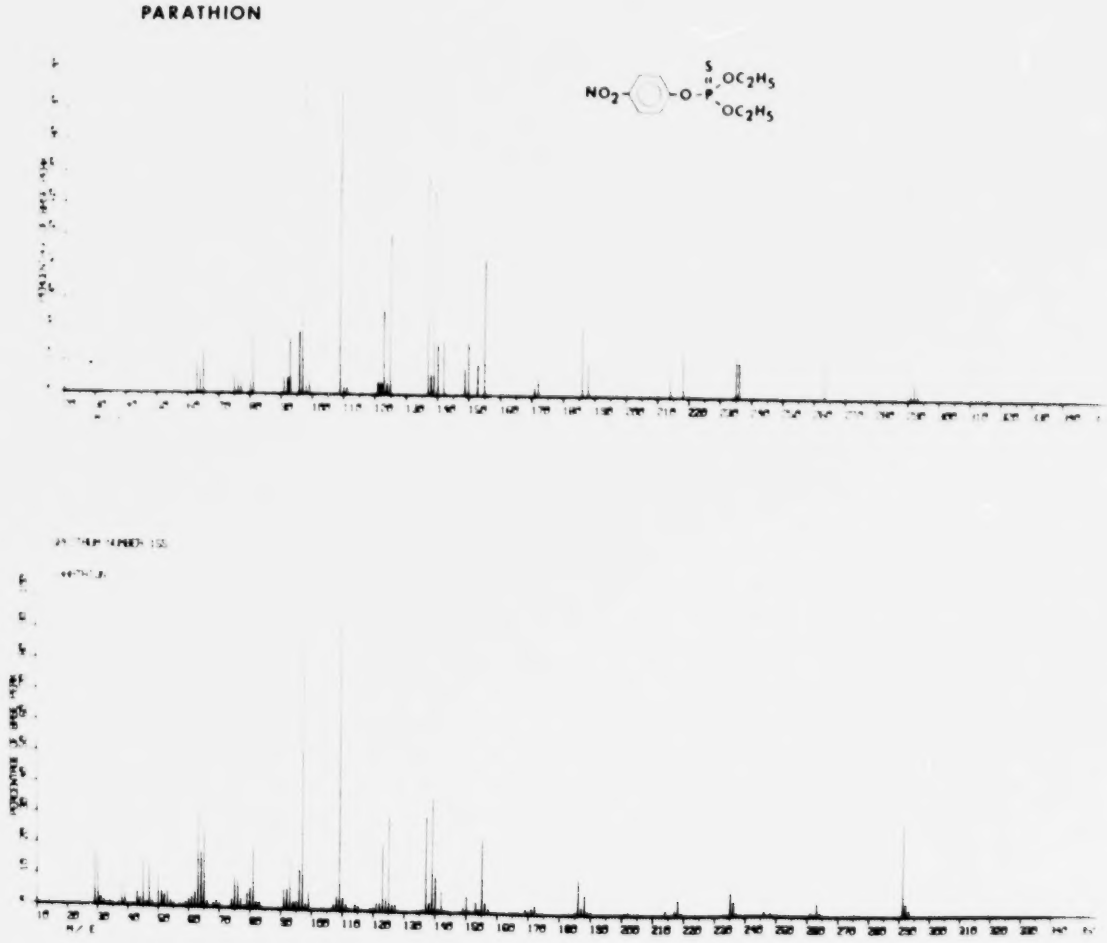


FIGURE 2. Comparison of parathion spectrum from a) magnetic instrument and b) quadrupole instrument

spectrometers, a major concern in the development of the matching system was whether suitable matches could be obtained between quadrupole and magnetic deflection spectra. Experience with the system has shown that the program provides excellent matches.

In one study made at the Southeast Environmental Research Laboratory, 50% of the unknowns present in the effluent of a Kraft paper mill were found correctly as the best hit, 8% as the second best hit, and 2% as the third best hit (13). The success of the system should improve since reference spectra are added continually.

SECTION IV

SPECIFIC POLLUTANT IDENTIFICATIONS

Examples are presented to illustrate the use of GC/MS for specific identifications of environmental pollutants.

Manual GC/MS

One project of the Southeast Environmental Research Laboratory involves the identification of pollutants from the textile industry. As part of this research, A. W. Garrison (14) utilized manual GC/MS methods to identify two pollutants and track them from their source in a carpet yarn mill to the water intake of a town six miles away. The flame ionization chromatogram of an extract of water from the receiving creek showed one major peak and many small ones. Only the two peaks labeled in Figure 3 were identified. From its mass spectrum, the major peak was identified as p-nonylphenol, a degradation product of a surfactant used in the fibre dying process. The second peak was identified by flame ionization chromatography as dieldrin, a moth-proofing compound known to be used in the plant. Mass spectrometry confirmed the identification.

Computerized GC/MS

The effluent of a pesticide manufacturing plant was monitored by GC. It contained low concentrations of several chlorine-containing pesticides and much higher concentrations of other chlorinated organics with relative retention times different from those of known pesticides.

The sample was analyzed by low resolution GC/MS operated under computer control. The reconstructed gas chromatogram (RGC) shows 31 peaks (Figure 4). Fourteen of these (Table 3) were identified generically as chlorinated hydrocarbons of which 13 were identified specifically. The 13 spectra (Appendix I) were included in the EPA/Battelle reference file.

Preceding page blank

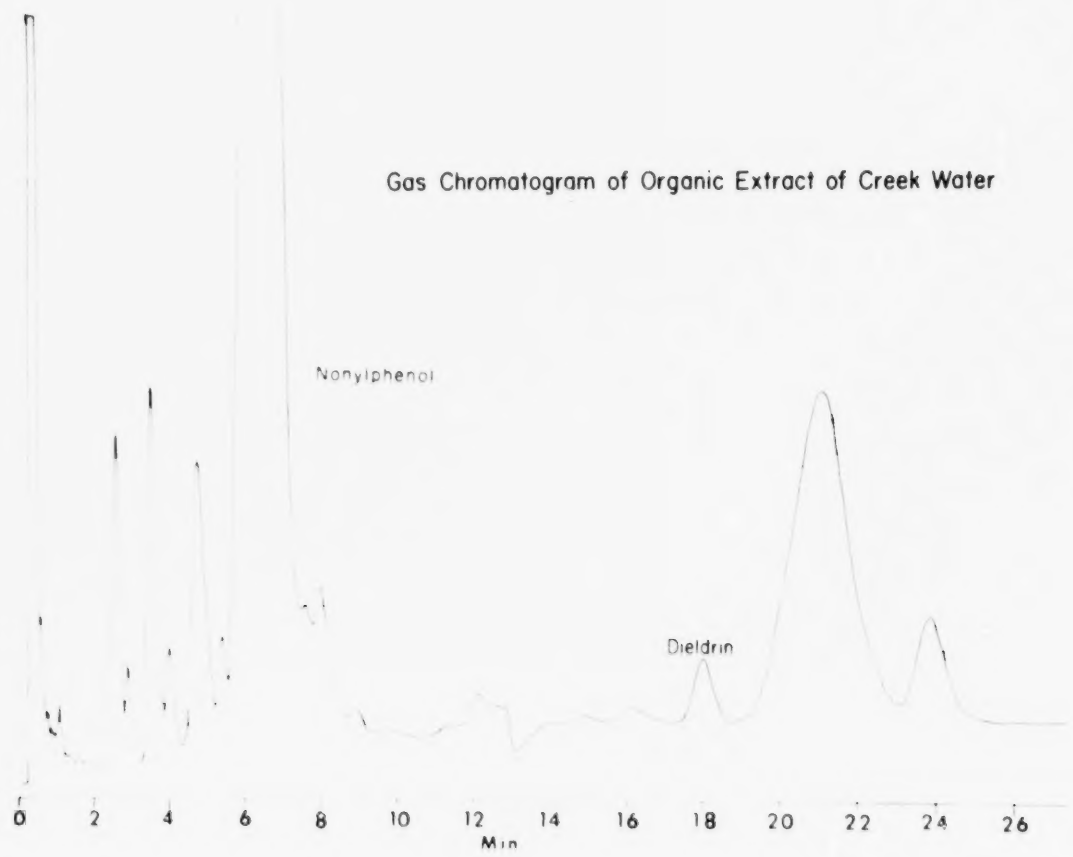


FIGURE 3. Flame ionization chromatogram of water extract

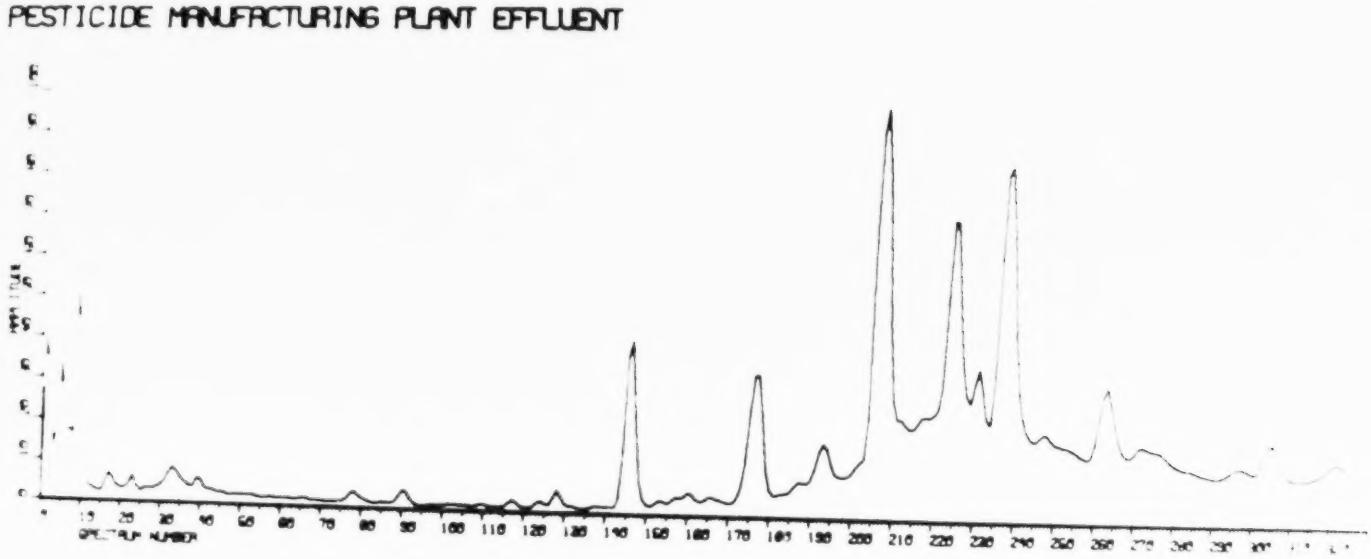


FIGURE 4. Reconstructed gas chromatogram of pesticide manufacturing plant effluent

Table 3

Compounds Identified in Pesticide Plant Effluent

trichlorocyclopentene isomer
hexachlorobutadiene
hexachlorocyclopentadiene
hexachloronorbornadiene isomer
octachlorocyclopentene
heptachloronorbornene isomers (2)
chlordene
heptachlor
1,2-epoxy-4,5,6,7,8,8a-hexachloro-4-
dicyclopentadiene (hexachlor epoxide)
chlordane
nonachlor
endrin
isomer of endrin (not specifically identified)

Electron capture gas chromatography of an extract of the effluent from another plant indicated the presence of polychlorinated biphenyls (PCB's) at concentrations of less than 1 µg/ℓ. An initial run on the low-resolution mass spectrometer gave the RGC shown in Figure 5. The major peaks below spectrum 15 were readily identified as chlorobenzenes and monochloro-biphenyls. On the basis of their mass spectra, peaks with longer retention times were judged to be due to chlorinated biphenyls; however, high background in this run prevented us from obtaining an RGC comparable to the chromatogram obtained with the electron capture detector, which is relatively more responsive to the chlorine-containing peaks. A limited mass reconstructed gas chromatogram, (LMRGC) covering the major PCB molecular ion peaks, would have permitted the comparison, but the presence of background ions interfered with some major PCB peaks.

To circumvent this interference, blank scans were made at highest instrument sensitivity to determine all significant background ions. In a second data acquisition run, all significant peaks noted in the blank were ignored by the computer. A limited mass reconstructed gas chromatogram, obtained from these data for the hexachlorobiphenyl

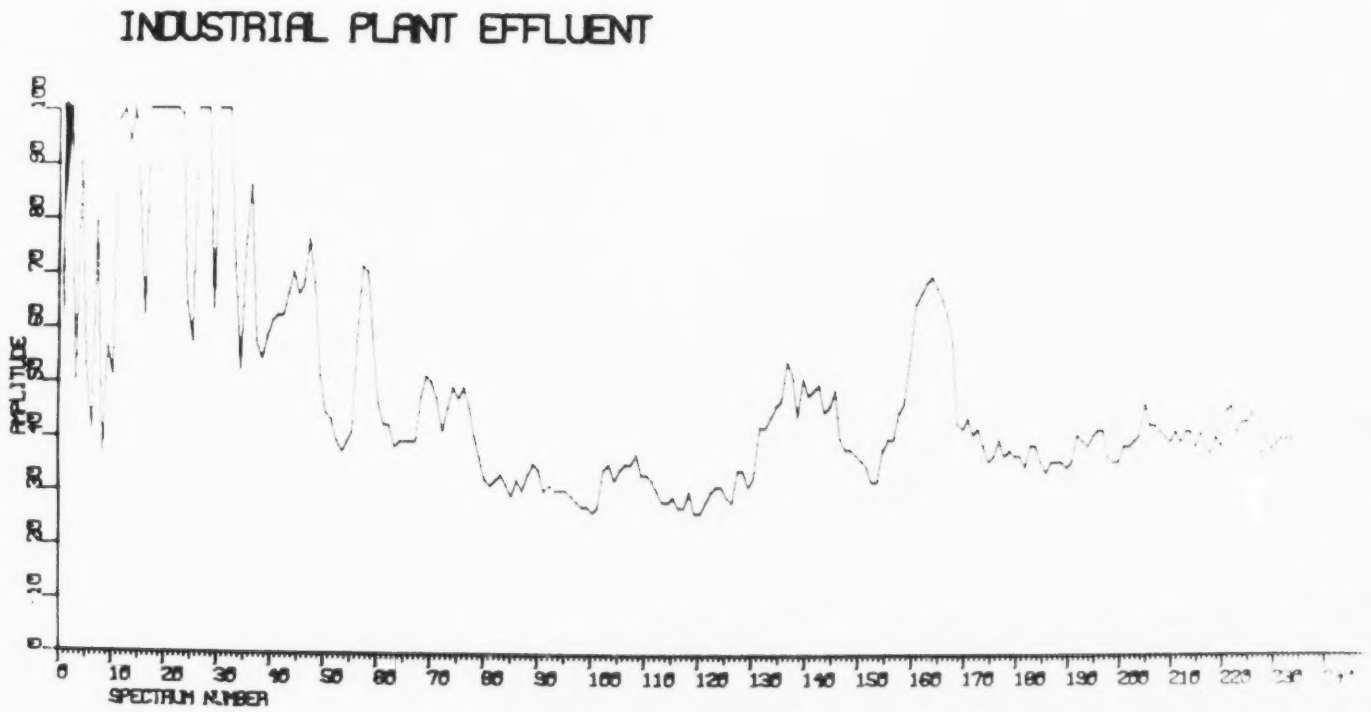


FIGURE 5. Reconstructed gas chromatogram of plant effluent containing polychlorinated biphenyls

region (Figure 6), was comparable to the electron capture detector chromatogram. Based on this comparison and the chromatographic data, the suspected material was identified as Aroclor 1260.

Computerized GC/MS and Spectra Matching

To check the practicality of computerized spectra matching as a means of identifying trace contaminants in the environment, a synthetic mixture of four pesticides was prepared. Atrazine, sevin, parathion, and p,p'-DDT were dissolved in an organic solvent at concentrations equivalent to those that would have resulted from extraction of a water sample containing them at concentrations of 1 µg/ℓ. The RGC (Figure 7) of this mixture showed a high background. The DDT spectrum (Figure 8) was typical of the spectral quality of the run. As shown by the S.I.'s in Table 4, good matches were obtained by the EPA/Battelle computerized spectra matching program.

Table 4

Identification of Trace Components in Synthetic Pesticide Mixture

Component	Best Match	S.I.	Second Best Match	S.I.
Atrazine	Atrazine	0.478	None	--
Sevin	Sevin	0.510	Sevin	0.501
Parathion	Parathion	0.574	Parathion	0.220
p,p'-DDT	p,p'-DDT	0.352	p,p'-DDT	0.287

In a study of the effluent of an experimental coal gasification plant, organic components were extracted with methylene chloride. The RGC of the extract (Figure 9) contained seven distinct peaks.

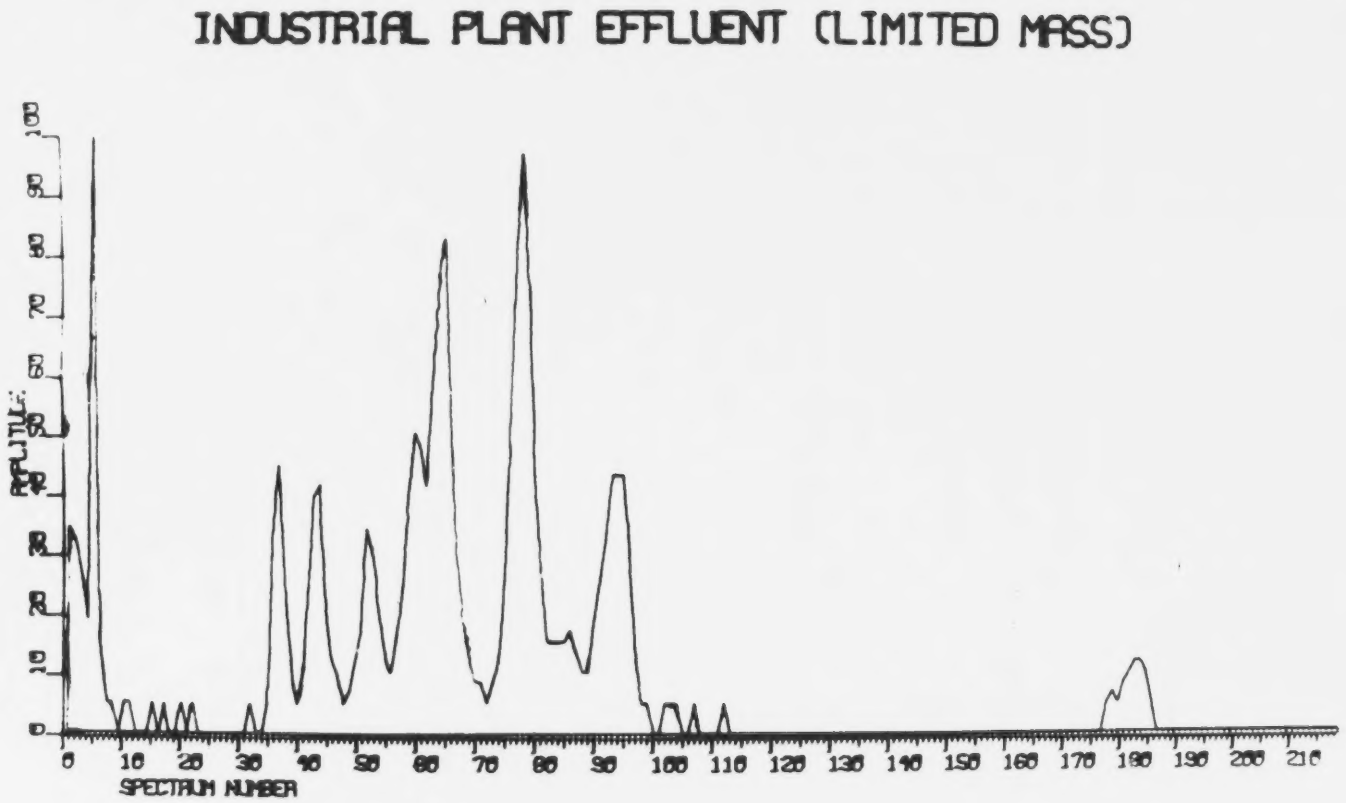


FIGURE 6. Limited mass reconstructed gas chromatogram of plant effluent containing polychlorinated biphenyls

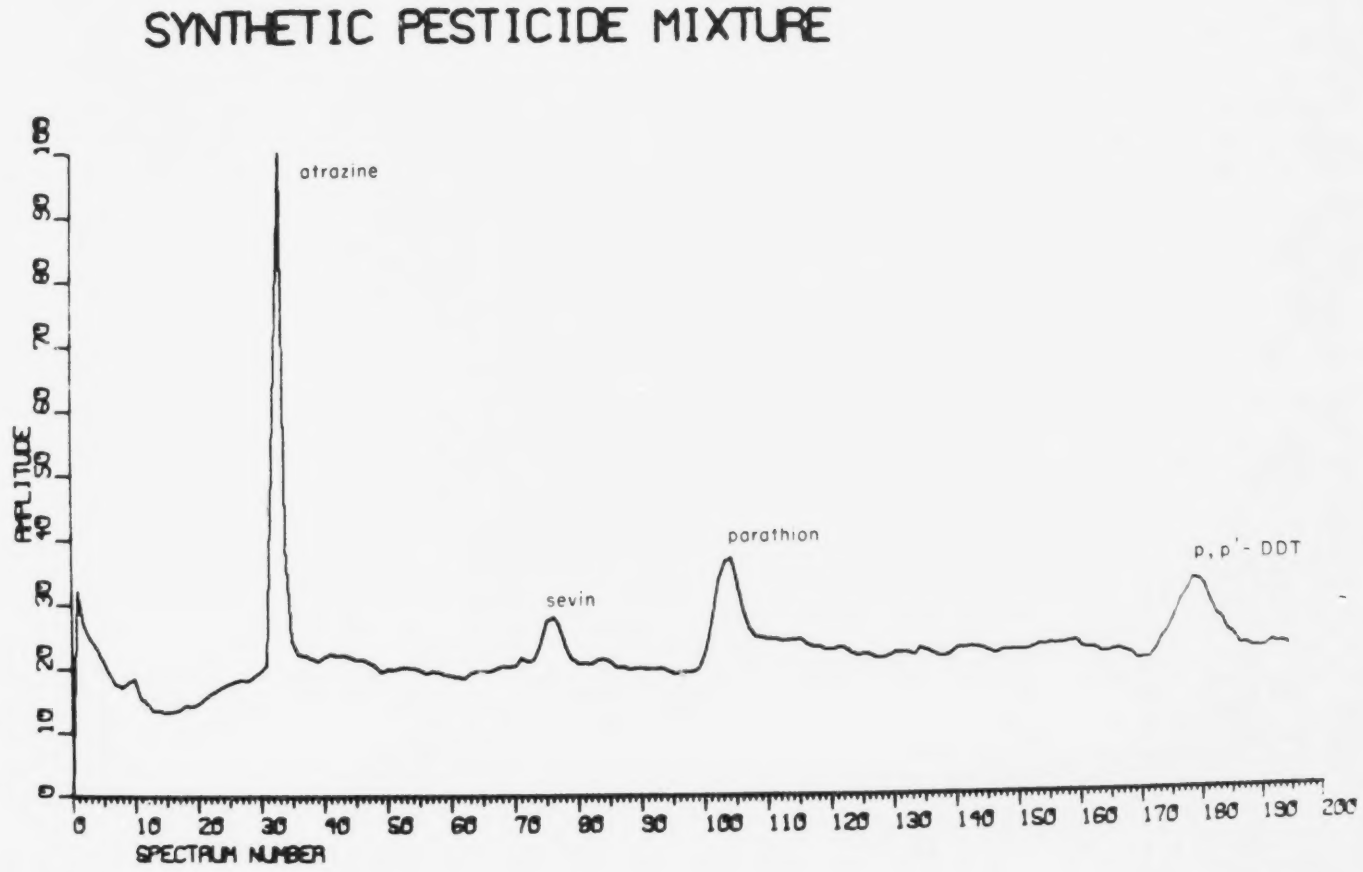


FIGURE 7. Reconstructed gas chromatogram of synthetic pesticide mixture

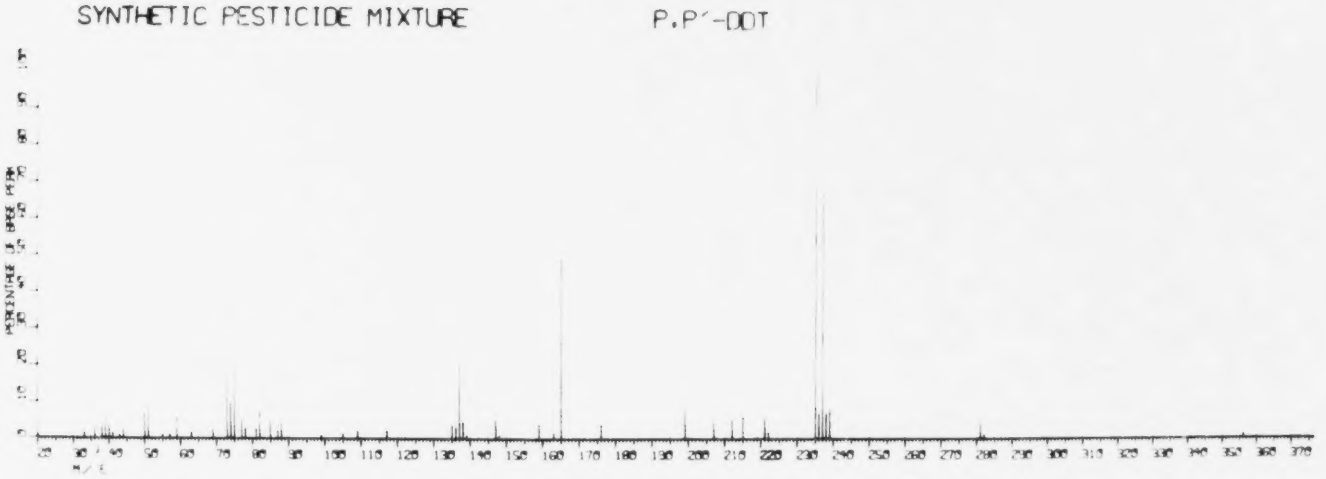


FIGURE 8. Mass spectrum of p,p'-DDT from synthetic pesticide mixture

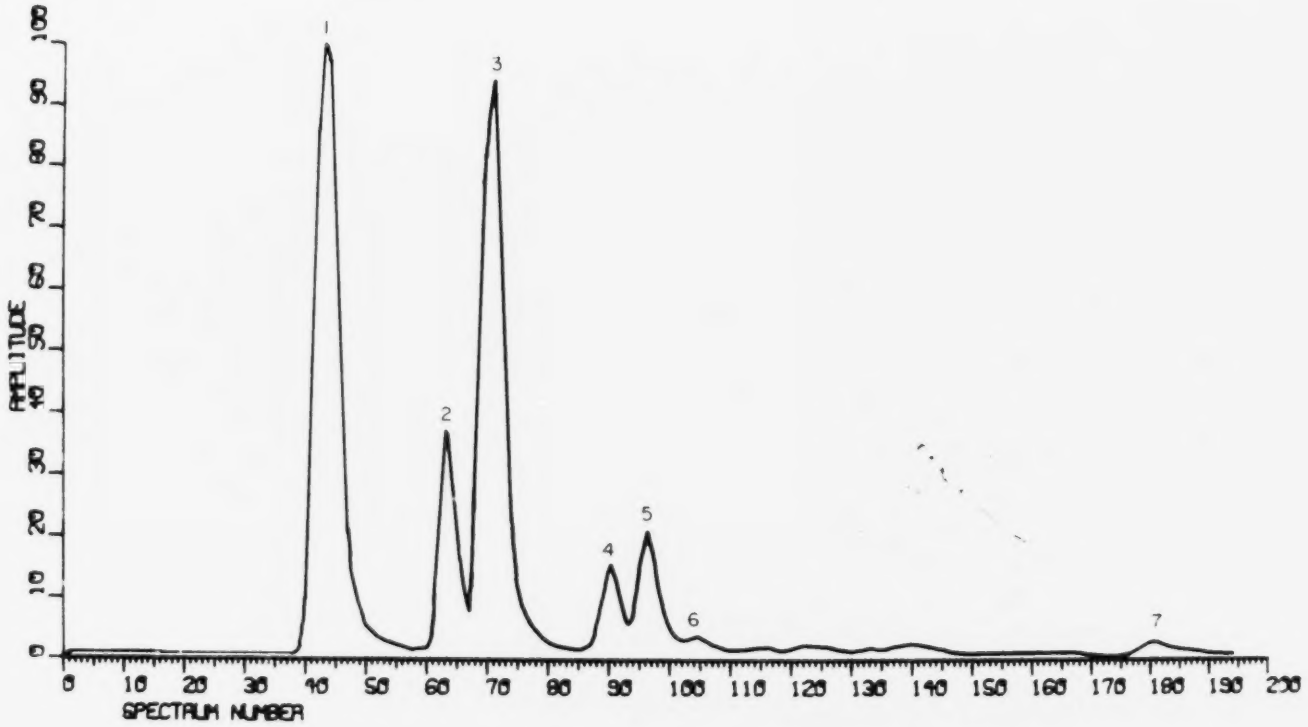


FIGURE 9. Reconstructed gas chromatogram of coal gasification plant extract

In a computerized matching of the spectra for those compounds, the best matches were with C_6, C_7, and C_8 hydroxyl-containing materials. High S.I.'s were indicated for the first six peaks, but a low one for the last GC peak. Subsequent visual inspection of the mass spectrum for this GC peak indicated that the last peak arose from two compounds with the same retention time.

The identifications are given in Table 5. When different materials were selected by the matching program as the best and second best matches, relative GC retention times favored the best match over the second best. In a continuation of the computer dialogue, given in Figure 10, for RGC peak 3, thirteen cresol spectra were matched with S.I.'s greater than 0.645. The first non-cresol match was 3-tolyl-N-methyl carbamate with an S.I. of 0.574.

Table 5

Compounds Tentatively Identified in Waste Effluent of Coal Gasification Pilot Plant

RGC Peak	Best Match	S.I.	Second Best Match	S.I.
1	Phenol	0.834	Phenol	0.795
2	o-Cresol	0.846	m-Cresol	0.741
3	m-Cresol	0.867	o-Cresol	0.842
4	2,5-Dimethyl-phenol	0.839	2,6-Dimethyl-phenol	0.804
5	3,4-Dimethyl-phenol	0.700	3,4-Dimethyl-phenol	0.692
6	2,4-Dimethyl-phenol	0.653	3,4-Dimethyl-phenol	0.637
7	α-Naphthol	0.245	1,2-dihydroxy-1,2-dihydro-naphthalene	0.232

```
[illegible], ØR P?S
I.D[illegible]AL GASIFICATION PLANT EFFLUENT
PAPE[illegible]?Y
[illegible]
CHPFI-1 (1S[illegible]
37,3;38,8;3[illegible],29;40,4;41,2;43,2;50,12;51,20;52,10;61;:
53,18;54,6;55,4;61,2;62,4;63,9;64,2;65,4;66,2;56;:
74,2;77,41;78,9;79,38;80,13;81,2;89,4;90,12;91,6;61;:
106,3;107,100;108,91;109,6;33;:
END

PARMTRS?  M100-500
111 HITS
M-CRESØL 108 C7.H8.Ø AST 0181
FILE KEY= 186
SI=0.857

1-HYDRØXY-3-METHYLBENZENE (3-METHYLPHENØL--M-CRESØL)
108 C7.H8.Ø TRC 0068
FILE KEY= 6392
SI=0.845

1-HYDRØXY-2-METHYLBENZENE (2-METHYLPHENØL--O-CRESØL)
108 C7.H8.Ø TRC 0067
FILE KEY= 6391
SI=0.834

1-HYDRØXY-4-METHYLBENZENE (4-METHYLPHENØL--P-CRESØL)
108 C7.H8.Ø TRC 0069
FILE KEY= 6393
SI=0.815

M-CRESØL 108 C7.H8.Ø AST 0459
FILE KEY= 462
SI=0.805
```

Figure 10. Computerized spectra matching program dialogue for a component of coal gasification plant extract

The present matching program depends on the presence in the reference library of the correct compound to identify an unknown. If the correct compound is not in the library, but closely related ones are, these materials will be identified as the most likely ones. At this point, inspection of matches and spectra frequently suggests the correct answers. In any case, identities should be confirmed by use of standards.

Analysis of the waste effluent of a synthetic rubber producer resulted in the RGC shown in Figure 11. This chromatogram shows four major peaks; however, satisfactory identifications by spectra matching were obtained for only two compounds. The second peak was found to be bis(2-chloroethoxy)methane (S.I.=0.63) and the fourth major peak was 1,2-bis(2-chloroethoxy)ethane (S.I.=0.676). Visual inspection of the spectra for the first and third GC peaks indicated that the compounds contained sulfur; however, no matches were obtained for compounds having molecular weights compatible with the molecular ion peaks of the spectra. We concluded that the first and third peaks were due to sulfur-containing compounds not included in the library.

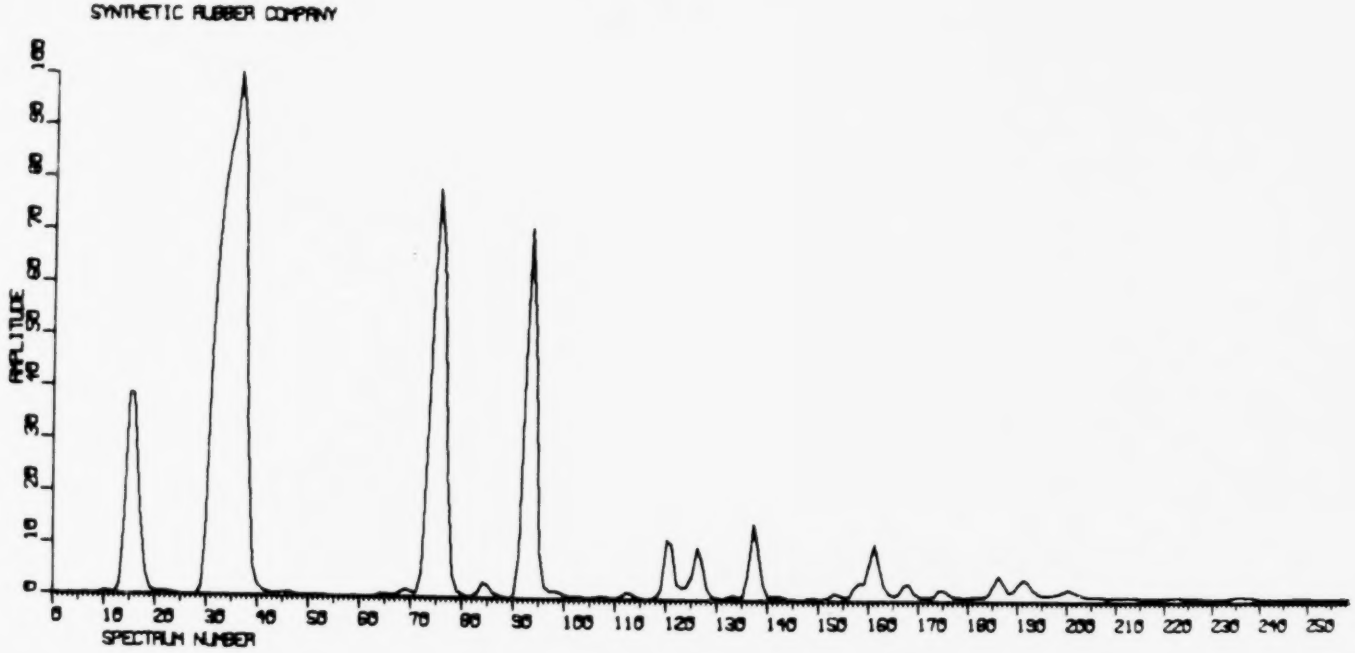


FIGURE 11. Reconstructed gas chromatogram of synthetic rubber plant effluent

SECTION V

ACKNOWLEDGMENTS

The authors acknowledge the data contributed by Dr. Lawrence H. Keith and Dr. Arthur W. Garrison of the Contaminants Characterization Program. Samples were provided by Mr. Donald Brown of EPA Region IV Chemical Services Branch, Dr. Warren Reynolds of EPA Region VI Chemical Services Branch, and Mr. A. G. Sharkey, Jr. of the U. S. Bureau of Mines, Pittsburgh, Pennsylvania.

SECTION VI

REFERENCES

1. L. H. Keith, A. W. Garrison, M. M. Walker, A. L. Alford, and A. D. Thruston, Jr., "The Role of Nuclear Magnetic Resonance Spectroscopy and Mass Spectrometry in Water Pollution Analysis," presented at the 158th National Meeting of the American Chemical Society, Division of Water, Air and Waste Chemistry, New York, N. Y., September, 1969.

2. A. W. Garrison, L. H. Keith, and M. M. Walker, "The Use of Mass Spectrometry in the Identification of Organic Contaminants in Water from the Kraft Paper Mill Industry," presented at the 18th Annual Conference on Mass Spectrometry and Allied Topics, San Francisco, California, June, 1970.

3. L. H. Keith, "Chemical Characterization of Industrial Effluents," presented at the 163rd National Meeting of the American Chemical Society, Division of Water, Air and Waste Chemistry, Boston, Massachusetts, April, 1972.

4. A. W. Garrison, L. H. Keith and A. L. Alford, Advances in Chemistry Series, No. 111, 27 (1972).

5. L. H. Keith and J. M. McGuire, "Computer-Controlled Mass Spectral Characterizations of Industrial Organic Pollutants," presented at the 164th National Meeting of the American Chemical Society, Division of Water, Air and Waste Chemistry, New York, N. Y., August, 1972.

6. B. G. Buchanan and G. L. Sutherland, Memo No. 62, Stanford Artificial Intelligence Report, July, 1967.

7. A. M. Duffield, A. V. Robertson, C. Djerassi, B. G. Buchanan, G. L. Sutherland, E. A. Feigenbaum, and J. Lederburg, J. Amer. Chem. Soc., 91, 2977 (1969).

8. J. Lederburg, G. L. Sutherland, B. G. Buchanan, E. A. Feigenbaum, A. V. Robertson, A. M. Duffield, and C. Djerassi, J. Amer. Chem. Soc., 91, 2973 (1969).

Preceding page blank

9. B. S. Finkle, D. M. Taylor, E. J. Bonelli, J. Chromat. Sci., 10, 312 (1972).

10. S. R. Heller, Anal. Chem., 44, 1951 (1972).

11. H. S. Hertz, R. A. Hites, and K. Biemann, Anal. Chem., 43, 681 (1971).

12. J. R. Hoyland and M. B. Neher, Battelle Columbus Lab. Annual Report to Environmental Protection Agency, Project #16020 HGD, March, 1973.

13. L. H. Keith, Southeast Environmental Research Lab, Athens, Georgia, personal communication, 1973.

14. A. W. Garrison and D. W. Hill, Amer. Dyestuff Reporter, February, 1972.

SECTION VII

GLOSSARY

GC--gas chromatography, a separation technique based on the partition of materials between gas and liquid phases.

GC/MS--a union of GC and MS in which the chromatograph effluent passes directly into a mass spectrometer inlet.

LMRGC--limited mass reconstructed gas chromatogram, a computer output that shows the relative currents resulting from positive ions of particular mass-to-charge ratio reaching the mass spectrometer detector as a function of scan number.

MS--mass spectrometry, an identification technique based on the fragmentation of ionized materials.

RGC--reconstructed gas chromatogram, a computer output that shows the relative currents resulting from all positive ions reaching the mass spectrometer detector as a function of scan number. This plot usually resembles the chromatogram obtained in GC.

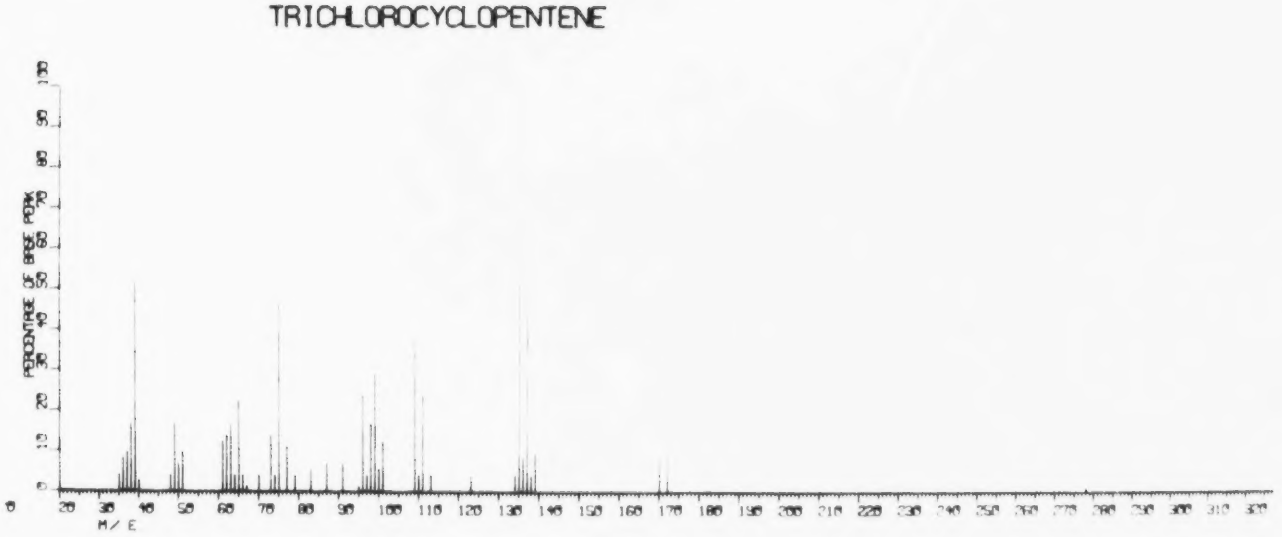
S.I.--Similarity Index, a numerical indication, ranging from zero to one, of how well an unknown spectrum matches a reference spectrum.

SECTION VIII

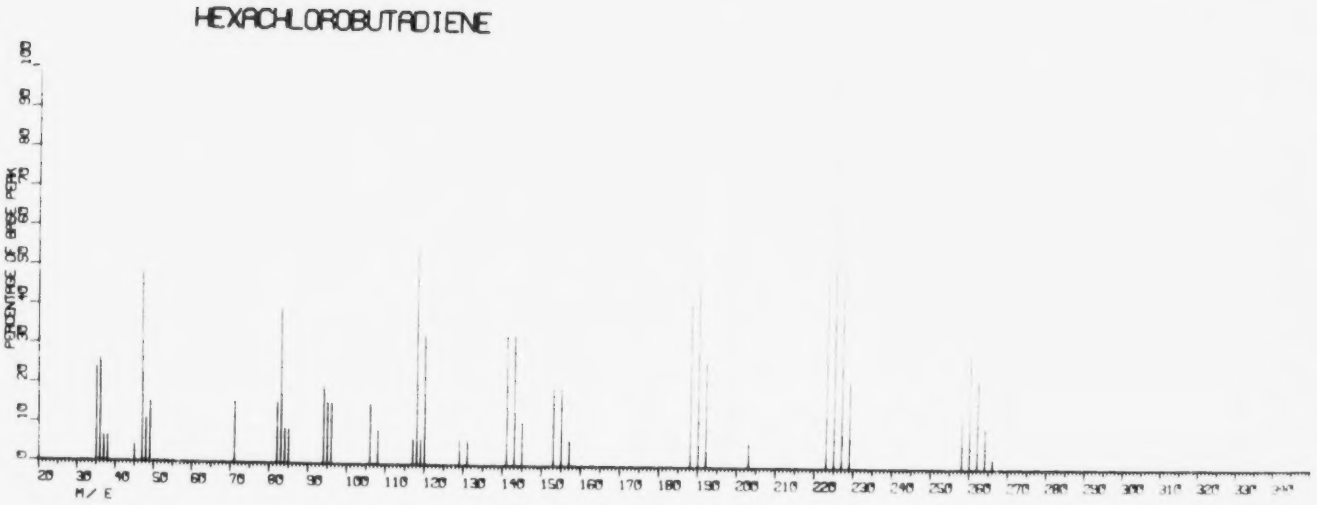
APPENDIX

Mass spectra of 13 compounds identified in pesticide manufacturing plant effluent.

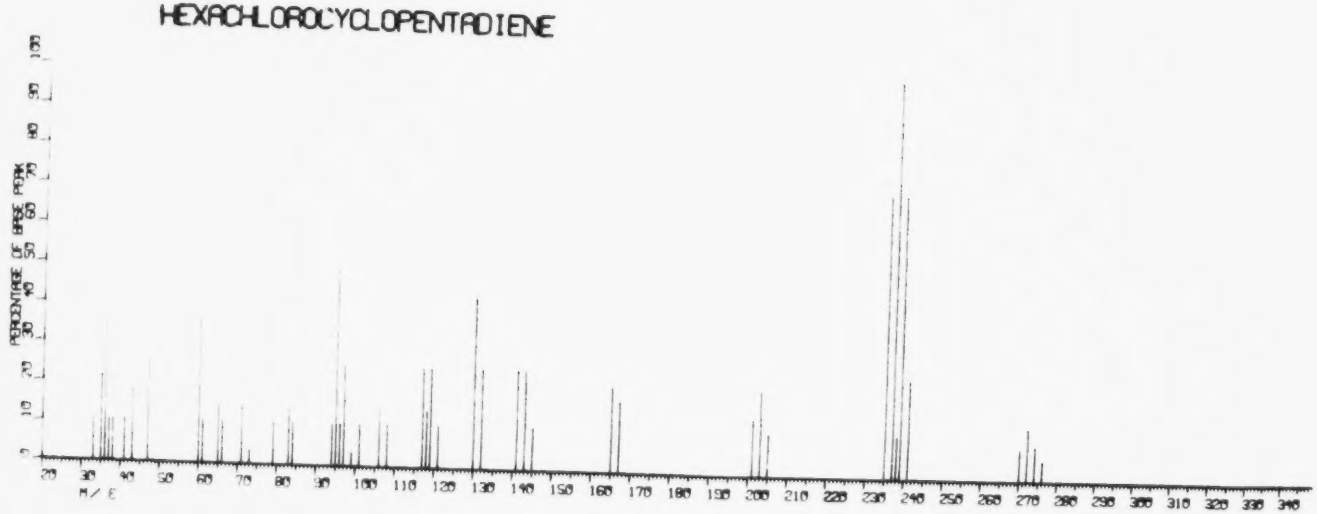
Preceding page blank



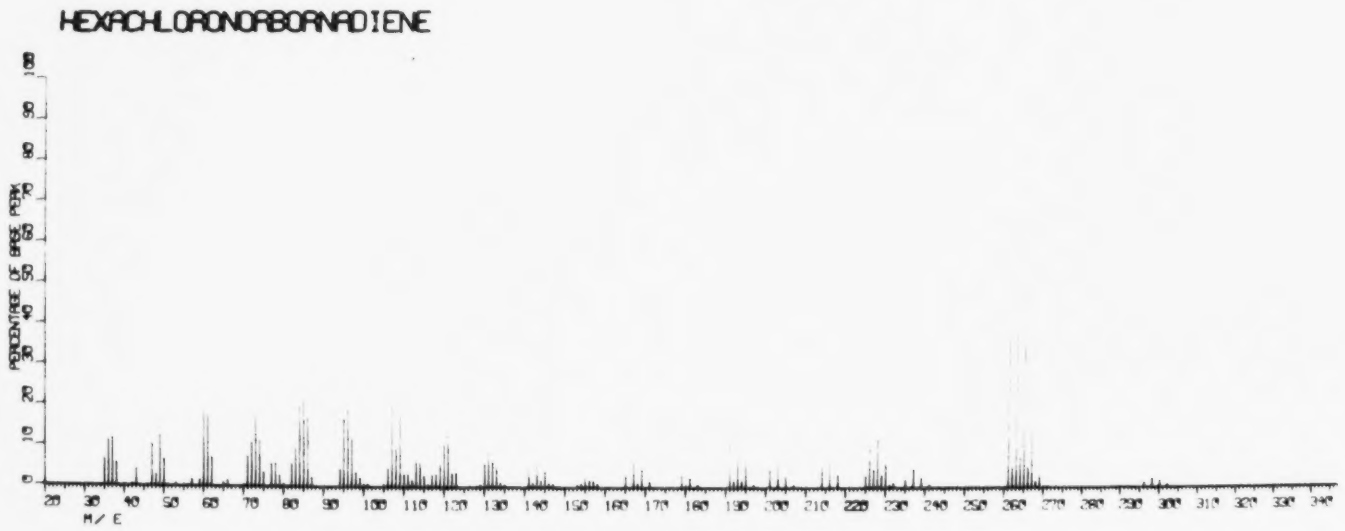
Mass spectrum of trichlorocyclopentene isomer



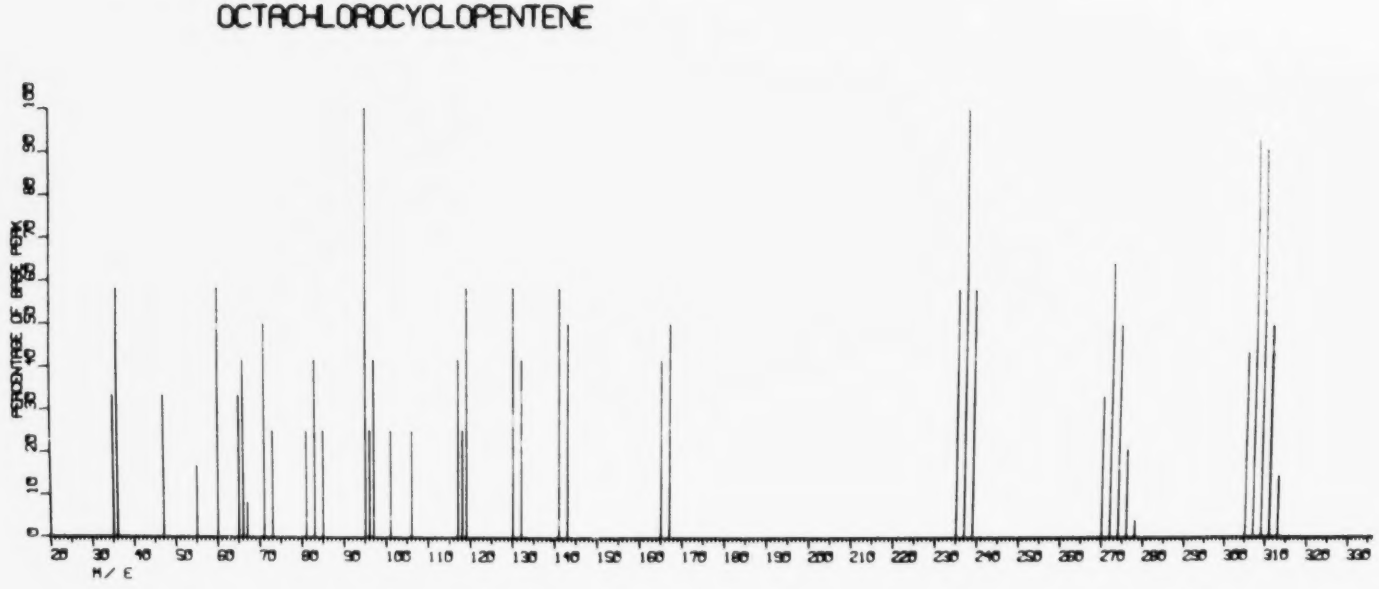
Mass spectrum of hexachlorobutadiene



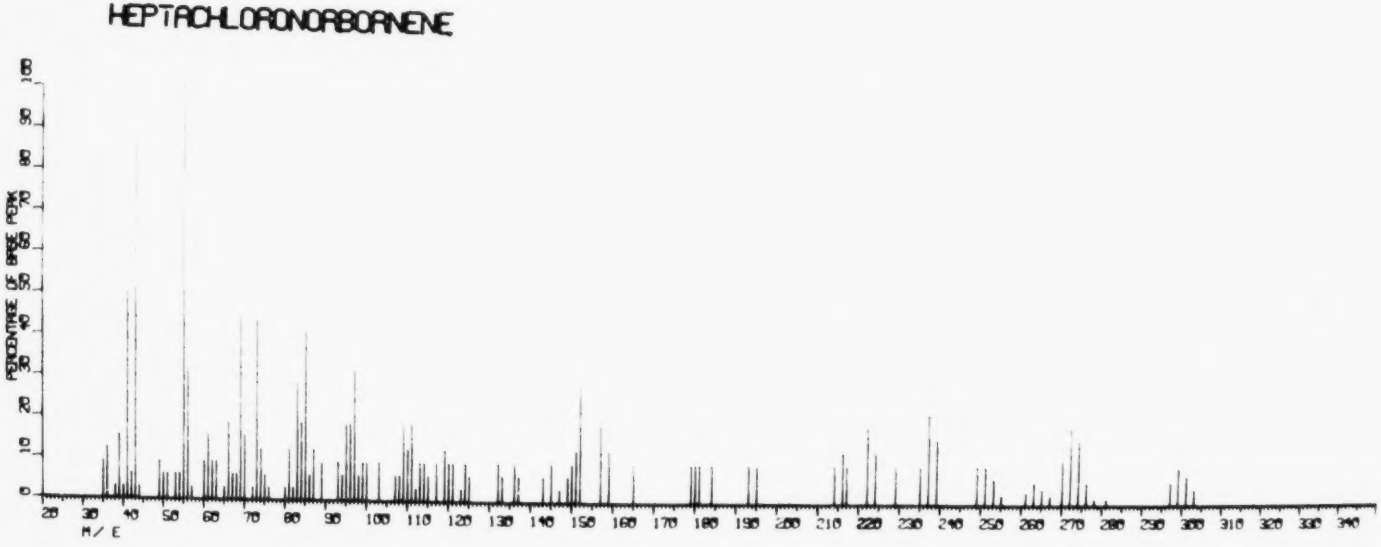
Mass spectrum of hexachlorocyclopentadiene



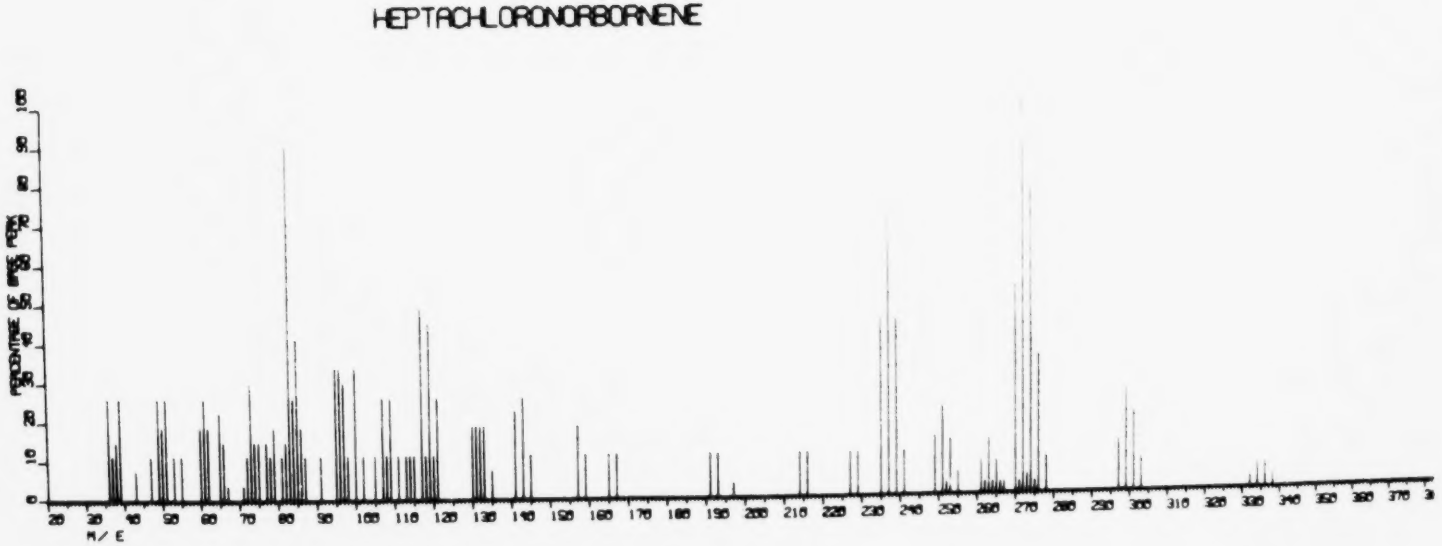
Mass spectrum of hexachloronorbornadiene isomer



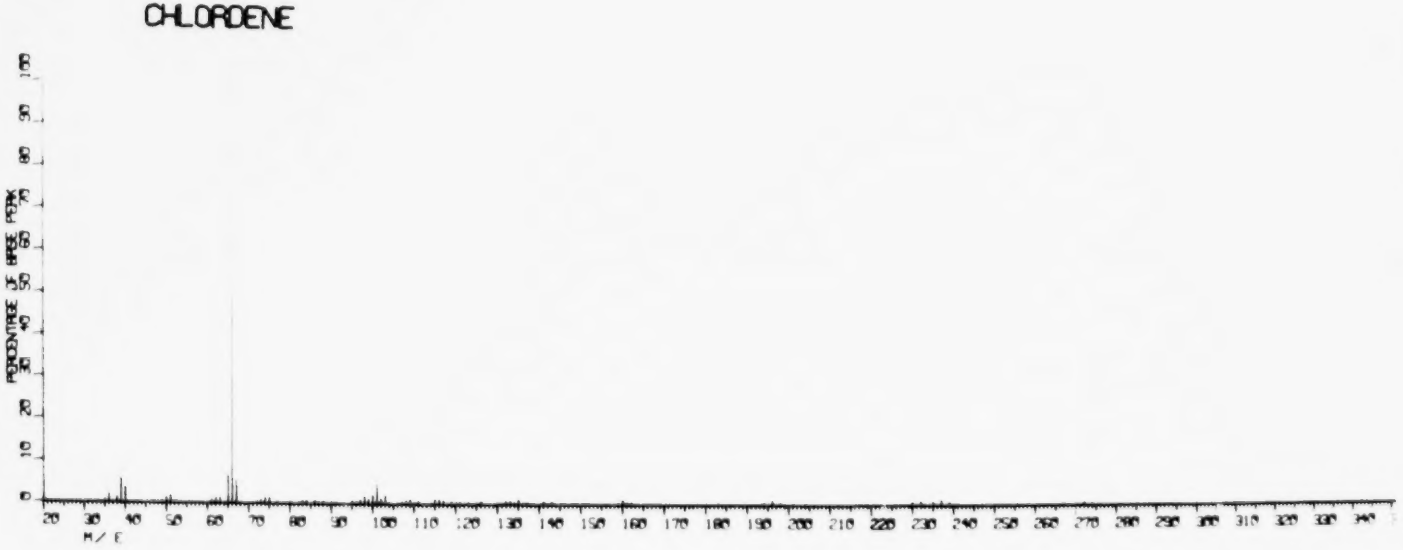
Mass spectrum of octachlorocyclopentene



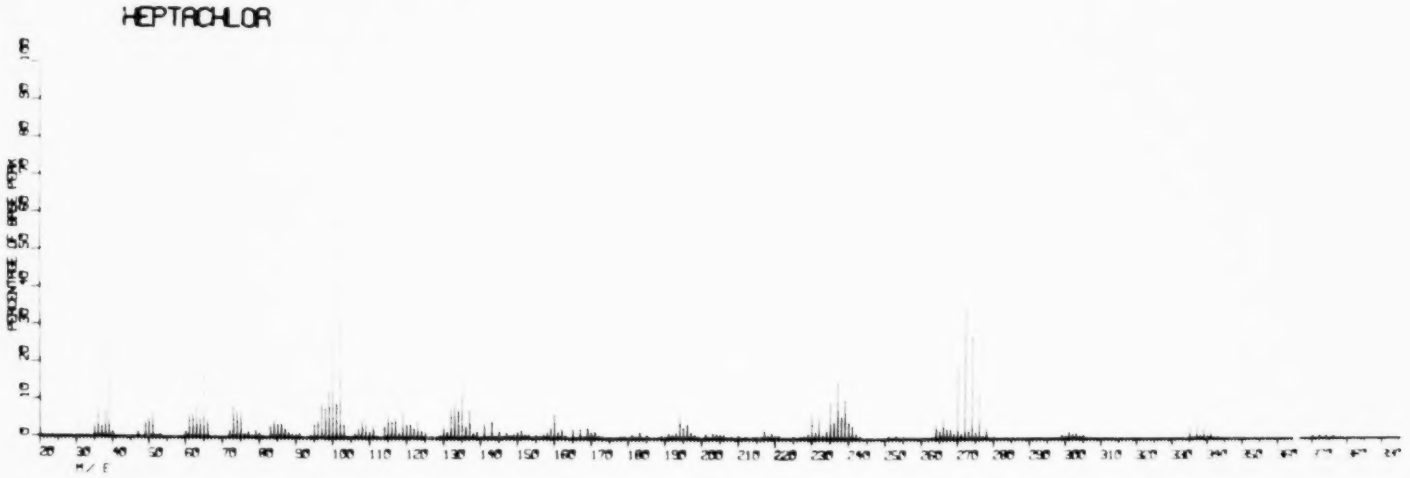
Mass spectrum of heptachloronorbornene isomer



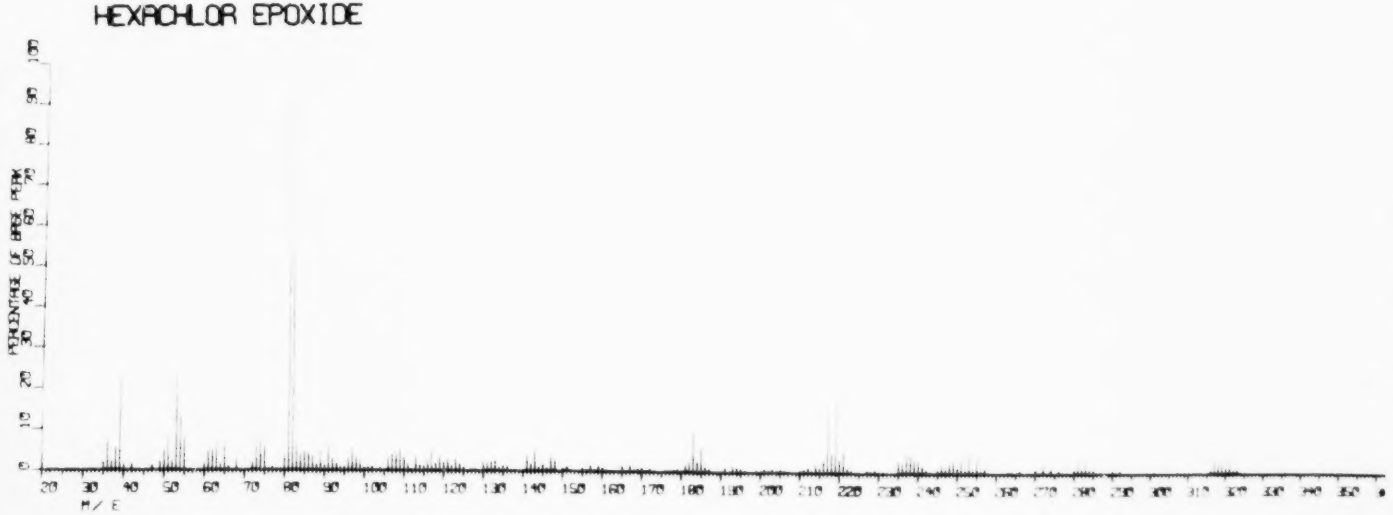
Mass spectrum of heptachloronorbornene



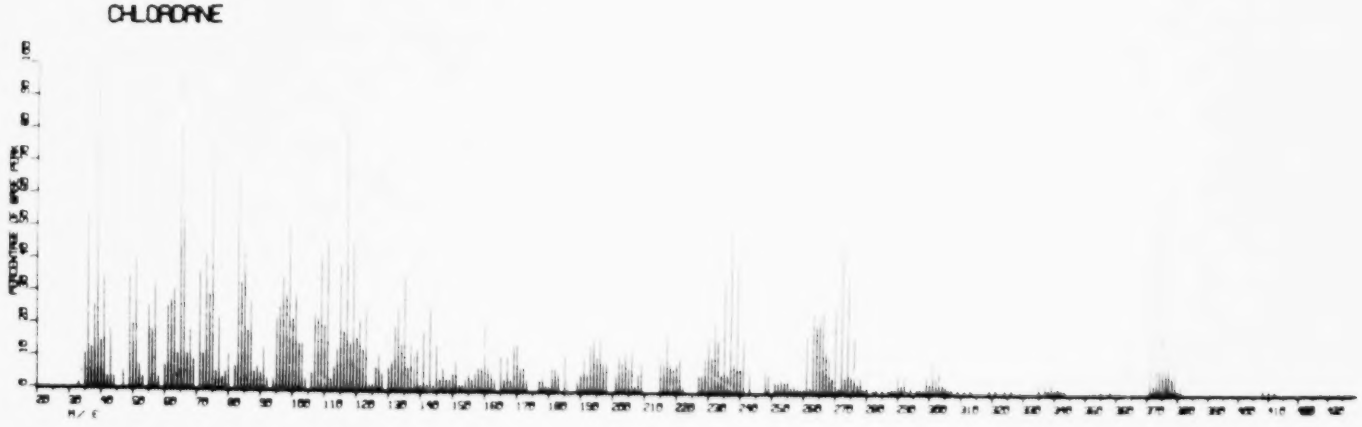
Mass spectrum of chlordene



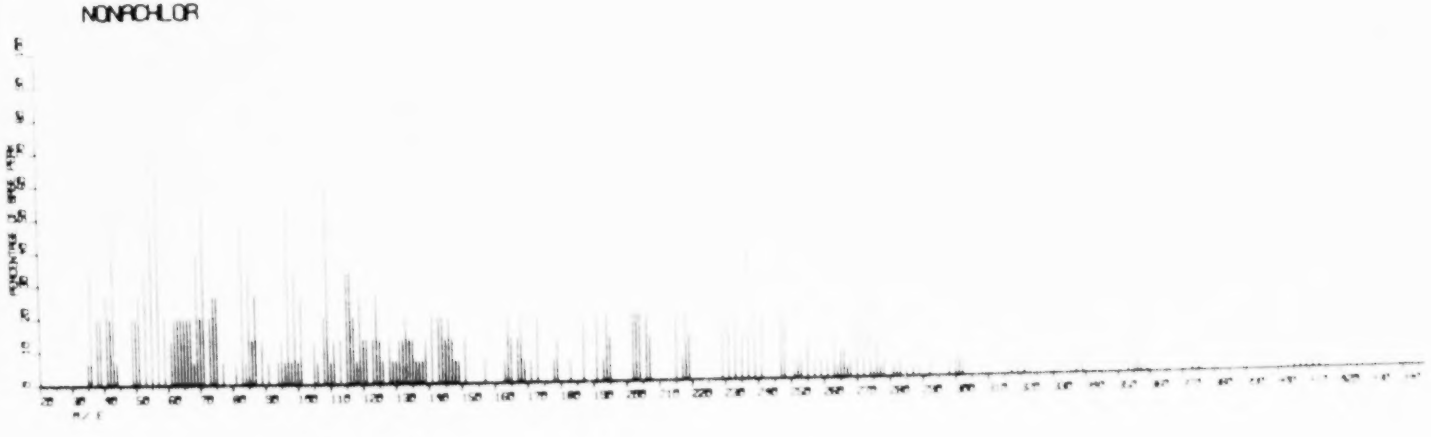
Mass spectrum of heptachlor



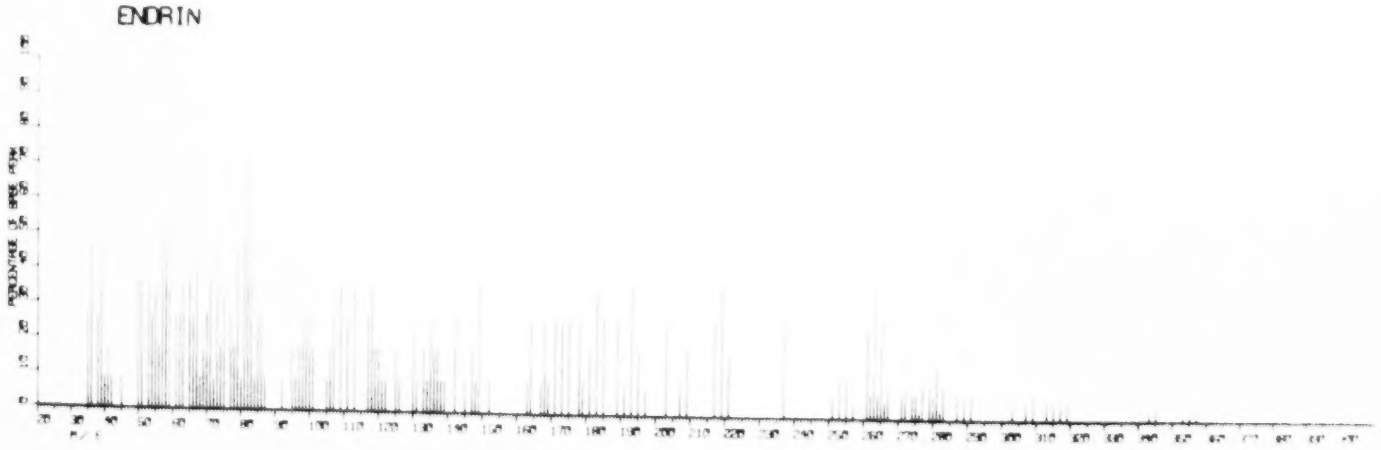
Mass spectrum of hexachlor epoxide



Mass spectrum of chlordane



Mass spectrum of nonachlor



Mass spectrum of endrin